STEM X-ray Analysis: Assessing the Past and Prophesying the Future

In Celebration of Steve Pennycook’s 60th Birthday

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*with lots of help from M. Watanabe, P. Kotula and M.G. Burke
A Selection of Analytical Electron Microscopes
Typical X-ray Analysis in the AEM*

*First proposed by Hillier and Baker, 1944
**ξ-Factor Method**

For element A:
\[ \rho t = \xi_A \frac{I_A}{C_A D_e} \]

For element B:
\[ \rho t = \xi_B \frac{I_B}{C_B D_e} \]

In binary system:
\[ C_A + C_B = 1 \]

**Thickness:**
\[ \rho t = \frac{\sum \xi_j I_j}{D_e} \]

**Composition:**
\[ C_A = \frac{\xi_A I_A}{\rho t} = \frac{\xi_A I_A}{\sum \xi_j I_j} \]

D<sub>e</sub>: total number of incident electrons

Intensity maps from $\text{Pb(Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$-35mol%PbTiO$_3$

**ADF-STEM**

Pb $L\alpha$

O $K\alpha$

**Quantified composition maps**

**Thickness**

Pb

O


*Coslett and Duncumb 1956*
Spectrum Imaging (SI) in (S)TEM*

Spectrum imaging (SI): a mapping technique to collect the whole spectrum at individual pixels

- STEM-XEDS SI
- STEM-EELS SI
- EFTEM SI

Advantages
- Less chance to miss minor peaks
- Post-acquisition processing
- Potential capability for regular spectral processing

*First performed by Legge and Hammond, 1979
SI X-ray Maps from a Ni-base Superalloy

Maps of minor elements are very noisy.
Multivariate Statistical Analysis

Multivariate analysis is the simultaneous statistical consideration of relationships among many measured properties.

“The techniques are not at all conceptually difficult......
But practical utility requires immensely long computations....”

Results of PCA 1

STEM-ADF

Score

Loading

#1: average

#2: M_{23}C_{6}

#3: \gamma'

200 nm

scree plot

Eigenvalue

Component

STEM-ADF

Score

Loading
Results of PCA 2

STEM-ADF

Score

Loading

Scree plot

Component

Eigenvalue

200 nm

#4: absorption

#5: noise

#6: noise
Application of MSA to Weak XEDS Signal

Nb map in Ni-base superalloy

Creating something out of nothing – note full scale of composition range
Elemental Maps at Atomic Resolution

HAADF-STEM

Ga (intensity)  As (intensity)  Overlay (Ga, As)

Ga (at%)  As (at%)  thickness (nm)

Average:
Ga: 50.8 at%
As: 49.2 at%
t: 38.1 nm
Low Resolution X-ray Mapping

Precipitate composition

From XEDS map:
Ni: ~30 wt%, Mn: 4-5 wt%, Cu: 4-5 wt%

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Corrosion Fatigue of Type 304 SS

Differences in Corrosion Fatigue Crack Growth Rates – Dependent on S content... Why/How?

Titan S, Cr, O EDX SDD Spectrum Images showing localised S enrichment at the crack-tip crack wall

EBSD orientation map (grains, evidence of strain, oxide identification)

MG Burke, A Gholinia, SHaigh, NPlatts, D Tice

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Most engineering problems are not in the noisy atoms
The future is in the (lower magnification) images

Thank you